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POLAROGRAPHIC DETERMINATION OF METALS IN LUBRICATING OILS

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For performance tests of different lubricating oils, as one of the means of estimating engine wear the method of constructing a curve of engine wear according to the content of iron in the oil used in operation is applied. However, to base the characteristic of engine wear only on the presence of iron in the waste oil is inadequate, since bearings of easily corroded non-ferrous metal alloys are used in modern engines. In the case where bearings of lead bronze are used the estimation of engine wear should be based on the content of iron, lead, and copper in the oil; in the case of babbitt bearings, on the content of iron, lead, and tin.

In this connection there arose the question of working out a method of determining iron, copper, lead, and tin in lubricating oils. For the quantative determination of these metals in lubricating oils we settled on the polarographic method, which permits these metals of interest to us to be determined quickly and with sufficient accuracy.

The polarographic method has been employed by certain Soviet researchers for the determination of one or several metals in oils (1, 2, 3, 4). However, the conditions recommended in certain works for the extraction of the metals from oil, as well as the conditions for the polarographic determination of them in the testing did not seem sufficiently reliable. Therefore, we conducted a systematic investigation through the study of the conditions for the polarographic determination of metals when they are simultaneously present in oil, and also the conditions for the extraction of the metals from oil.

EXPERIMENTAL PART

The polarograms were taken on the visual polarograph ME-500 (1945 model) of the Institute of Chemistry at Gor'ky State University.

A galvonometer whose sensitivity was $6.6 \cdot 10^{-9}$ amp/mm at a scale distance of 25 cm from the mirror served for measurement of the current. The capillary constant $m^{2/3}t^{1/6}$ was equal to 1.90 $mg^{2/3}sec^{-1/2}$. As the anode a saturated calomel electrode was used which was connected with the solution under investigation by means of an agar-agar bridge.

Determination of Iron

Prior to the determination of iron, hydrochloric acid of different concentrations and also citric acid in a weakly ammoniacal solution (the latter reagent forms a complex with iron (5)) were tested as polarographic carriers. From the experimental data it was ascertained that a 1.2 N solution of hydrochloric acid serves as the best electrolyte for the determination of iron (especially in the presence of lead).

The wave of iron appears at the very beginning of the polarogram, and the height of the wave is calculated from the zero value of the potential.

To verify the accuracy of the method of extraction of iron from oil, the following comparative tests were conducted:

1) extraction of iron with hydrochloric acid under the conditions recommended by Korshunov and Shchennikov (3).

2) the method of dry ashing of the oil with the subsequent extraction of the metallic oxides with hydrochloric acid.

In the first method iron, added to 20 g of oil in metallic form, was extracted with hydrochloric acid 1:1 containing an admixture of a small quantity of nitric acid. To obtain a quantitative recovery of iron the extraction with 1:1 hydrochloric acid was repeated 3 times. The chloride extract obtained was evaporated to a smaller volume. The solution was poured

into a 100 ml measuring flask and the full volume attained by adding water up to the mark; 10 ml of the solution were transferred into an electrolyzer for polarographic determination, hydrogen was passed through for 20 minutes, and a polarogram was taken. The data we obtained (Table 1) shows that the method of extraction does not lead to a full recovery of iron.

In this connection we checked the possibility of the quantitative recovery of iron after dry ashing, a weighed portion of the oil being tested. For this purpose experiments were conducted on the combustion of 20-25 grams of solvent-refined Avtol [automobile oil] "10" to which were added different quantities of iron. The oil was first carefully evaporated, and then the residue was burned in a muffle furnace at a temperature of 500°. The ashes were dissolved in 5 ml of concentrated hydrochloric acid, ~~and~~ the solution was transferred to a 50 ml measuring flask and the volume brought up to the mark by adding water. 10 ml of the solution were placed in the electrolyzer, hydrogen (electrolytic) was passed through for 20 minutes, and the polarogram was taken. The concentration of iron in the solution was determined from the graduations on the polarographic graph, and the iron content in grams was calculated for 1 gram of oil. The results are shown in Table 2, and the curve of one of the experiments in Figure 1.

Moreover, in certain specimens of waste oils the iron was determined after they were ashed by both the polarographic and colorimetric methods (the latter with sulfonylsalicylic acid) with the purpose of comparing the results obtained.

The data are shown in Table 3.

From the analysis of the data in Tables 2 and 3 it follows that: 1) the separation of iron from oil by the dry ashing produces fully satisfactory results; 2) the results obtained by the polarographic and colorimetric methods for determining iron in waste oils are in good agreement.

Determination of Lead

For the determination of small quantities of lead many investigators have used the polarographic method (6, 7, 8). Since in the scheme of analysis which we outlined iron, lead, and copper had to be determined from one weighed portion, we used as a carrier hydrochloric acid of the same concentration as for iron, i.e., 1.2N. The completeness of recovery of lead from the oil was verified when the ashing method was used, while the temperature of ashing in this case did not rise (was not raised) higher than 500°, since it was established experimentally that at a higher temperature losses of lead were possible. In this case artificial mixtures were prepared by the introduction into fresh oil of different quantities of lead corresponding to the usual content of it in waste oil. The oil was carefully evaporated and the residue calcined in a muffle furnace at a temperature not higher than 500°. The ashes obtained in this manner were dissolved in 5 ml of concentrated hydrochloric acid.

The solution was brought to exactly 50 ml in a measuring flask by the addition of water. Part of the solution was placed in the electrolyzer, hydrogen was passed through for 20 minutes, and the polarogram was taken.

In the polarogram a pronounced lead wave was obtained with a half-wave potential of -0.48 v relative to the saturated calomel electrode (see Figure 2). The lead concentration in the solution was found from the graduations on the polarogram and the content of lead calculated in grams per 1 gram of oil. The results obtained are shown in Table 4.

It follows from the data in Table 4 that the method for recovering lead by means of dry ashing of oil at a temperature not higher than 500° with its subsequent polarographic determination produces completely satisfactory results.

Determination of Copper

We reduced copper from a solution of 1 M ammonia and 1 M ammonium chloride which contained 0.008% joiner's glue and 0.2% sodium sulfite.

Calculations of the copper content was carried out by measuring the second wave, whose half-wave potential was equal to -0.45 v relative to the saturated calomel electrode.

In order to ascertain the completeness of recovery of copper from the oil after dry ashing, there was conducted a series of measurements on artificially prepared mixtures containing 20 g of light oil (solvent-refined Avtol "10") and different quantities of copper. The oil was carefully evaporated and then burned in the muffle furnace at a temperature not higher than 500°. The ashes were dissolved in 2-3 ml of concentrated hydrochloric acid and the solution transferred into a 50 ml measuring flask. The solution was neutralized with ammonia (with the aid of litmus), and then an excess of ammonium ions(ammonium chloride, sodium sulfite and joiner's glue) was added up to the above-specified concentration mentioned above. The solution was filled up to the mark, 10 ml of the solution were placed in the electrolyzer, and the curve was taken. The concentration of copper was found from the graduations on the polarogram and the copper content calculated in grams per 1 gram of oil. The results of the analysis are shown in Table 5, and the curve for one of the experiments in Figure 3.

From Table 5 it follows that the recovery of copper after ashing, with the subsequent polarographic determination of it, produces completely satisfactory results.

Determination of Tin

In view of the fact that when oil containing tin is ashed a difficultly soluble dioxide of tin is formed, the method of extraction of the oil with hydrochloric acid was used for the separation of tin. The completeness of

the recovery of tin was tested on artificially prepared mixtures composed of 50 gram weight portions of oil and different quantities of added tin. To the mixture, which was placed in a flask with a reflux condenser, 90 ml of 1:1 hydrochloric acid were added and the mixture heated in a water bath with frequent agitation for 1 hour. Then, after cooling, the hydrochloric acid solution was separated from the oil in a separatory funnel. The operation of extraction of the oil was continued for 2 more hours with 50 ml of 1:2 hydrochloric acid; after this the oil in the separatory funnel was washed with 50 ml of hot distilled water. After the first extraction the hydrochloric acid extract was placed in a 100 ml measuring flask, and those from the two subsequent extractions were placed together with the washing water in a porcelain dish; 1 ml of sulfuric acid was added, the solution in the dish was evaporated to minimum volume, combined with the original hydrochloric acid solution in the measuring flask, and water was added up to the mark.

10 ml of the solution were placed in the electrolyzer, hydrogen was passed through the solution for 20 minutes, and the polarogram taken. Here a pronounced wave appeared with a half-wave potential of -0.45 v in relation to the saturated calomel electrode (Figure 4).

The concentration of tin in the solution also was determined from the graduations on the graph and the tin content calculated in grams.

From Table 6 it follows that in the extraction of tin from oil with hydrochloric acid less accurate results are obtained. The error here does not exceed 12% for separate experiments, and on the average is equal to $\pm$ 6.8%.

Determination of Iron, Lead, and Copper When They Are Jointly Present in Oil

As has already been shown, in the case when bearings of lead bronze are used in an engine, the estimation of the wear of the engine must be made from the content of iron, lead, and copper in the waste oil.

The determination of each of these elements has been described above.

For the joint presence of these elements the method must be somewhat varied. In order to recover these metals from the oil, we employed the method of the dry ashing of the oil at a temperature not higher than 500°, the ashes being subsequently dissolved in hydrochloric acid. Iron and lead were separated from copper by precipitation with ammonia in the presence of ammonium chloride.

The precipitate of iron and lead hydroxides was filtered and washed with a weak solution of ammonia. The precipitate was then dissolved on the filter in 30 ml of a hot 2 N hydrochloric acid solution and the volume raised to 50 ml by dilution with water.

TEN
10 ml of the solution were placed in the electrolyzer, hydrogen passed through, and the polarogram taken. Here two waves were obtained on the polarogram: iron and lead. The content of each metal was determined from the graduations on the graph. To the filtrate, which contained copper, were added the wash solutions evaporated down to minimum volume, 2 ml of 10% sodium sulfite solution, and 0.4 ml of a 10% solution of joiner's glue; the volume was brought up to 50 ml with water. TEN 10 ml of this solution were placed in the electrolyzer and the polarogram was taken. The concentration of copper was determined from the graduations on the graph, and the content of copper was calculated for 1 gram of oil.

In Table 7 are presented the results of the determination of iron, lead and copper in artificially prepared mixtures.

From Table 7 it follows that for the determination of iron, lead, and copper in oil by the polarographic method after the ashing of a weighed portion of oil completely satisfactory results are obtained.

Determination of Iron, Lead and Tin in Oils When They Are Jointly Present

If babbitt bearings are present in engines, the waste lubricating oil can contain iron, lead, and tin. The accuracy of the quantitative extraction of these metals from oils was tested on artificial mixtures composed of oil into which were introduced specified quantities of metal. Iron and lead were recovered from the oil after it was ashed, and tin was extracted with hydrochloric acid. At this step lead was partially extracted. Since the reduction potentials of lead and tin are very close, their polarographic determination from the same solution is possible only after their separation. To separate tin from lead in the hydrochloric acid extract, 50 ml of the solution were withdrawn into a porcelain vessel, to which were added 2.5 ml of concentrated sulfuric acid. The solution was evaporated in a sand bath until sulfuric acid fumes appeared. After cooling, the walls of the vessel were washed with water and the solution was again evaporated up to the appearance of sulfuric acid vapors. 50 ml of water were added, and in an hour the precipitate of lead sulfate was filtered through an ash less filter; the precipitate on the filter was washed with a weak solution of sulfuric acid (3%) and the wash water added to the filtrate. The solution was evaporated almost to dryness, the residue dissolved in 40 ml of hot 1:1 hydrochloric acid, the solution transferred to a 50 ml measuring flask and enough acid of the same concentration added to bring the volume of the solution up to the mark. 10 ml of the solution were placed in the electrolyzer, hydrogen was passed through for 20 minutes, and the polarogram taken. In this case the precipitate of lead sulfate obtained on the filter was dissolved in 25 ml of a hot 20% solution of ammonium acetate, then washed with hot water, and the volume brough to 50 ml. Lead was determined directly in the amonium acetate solution.

The results are shown in Table 8.

From Table 8 it follows that the method for extracting lead and tin from oil with hydrochloric acid gives less accurate results. Therefore we recommend that lead be determined together with iron in oil ashes. As regards

tin, since a dioxide of tin which is difficultly soluble in acids is obtained when oil containing tin is ashed, (a dioxide which must be converted into a soluble product by melting) we applied the method of extraction in this case, although we do not consider it perfect.

After the conditions for carrying out the polarographic analysis and for isolating metals from oil were established, a large number of analyses of waste oils was conducted in order to determine the content of iron, copper, and lead in oil samples. On the basis of the data obtained, the wear of a motor was determined through the construction of a graph of wear. Certain results of the analysis are cited in Table 9.

As a result of the work carried on, the polarographic method for the determination of iron, lead, copper, and tin in oils was proposed as the All-Union State Standard GOST 4830-49.

Conclusions

1. A polarographic method was worked out for the determination of iron, lead, copper, and tin in oils which permits mass analysis of these metals in used oils to be carried out with satisfactory accuracy.

2. It has been shown that the recovery of iron, lead, and copper from oil after the dry ashing of it at a temperature not exceeding 500° gives more accurate results than the direct recovery of these metals from oil by means of hydrochloric acid.

3. It has been established that in the determination of iron, lead, and tin in oils when they are jointly present, the iron and lead should be determined after the oil has been ashed, but the tin should be extracted from the oil with hydrochloric acid followed by subsequent separation of it from lead by means of hydrochloric acid.

4. The proposed polarographic method for the determination of metals in oils permits a graph of wear to be constructed. This is a procedure which gives positive results in tests on engines.

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Table 1. Polarographic Determination of Iron in Artificial Mixtures when it is Recovered from Oil by Extraction

No of Experiment	Quality of Oil	Iron in g per 1 g oil		Relative Error in %
		Introduced	Determined	
1	Avtol "6", solvent refined	0.00102	0.00081	-18.6
2	The same	0.00049	0.00037	-24.5
3	" "	0.00096	0.00072	-25.0
4	" "	0.00060	0.00050	-16.7
			Average	-21.2

Table 2. Polarographic Determination of Iron After the Ashing of the Oil

No of Experiment	Quality of Oil	Iron in g per 1 g oil		Relative Error in %
		Introduced	Determined	
1	Avtol "10", solvent refined	0.000930	0.000970	+4.3
2	The same	0.000370	0.000370	--
3	" "	0.000930	0.000960	+3.2
4	" "	0.000440	0.000460	+7.0
5	" "	0.000094	0.000091	-3.2
6	" "	0.000083	0.000084	+1.2
7	" "	0.000007	0.000007	--
8	" "	0.000066	0.000053	-3.7
			Average	±2.8

NOTE: In the table is cited only an insignificant part of all the experimental data.

Table 3. Comparative Results of the Polarographic and Colorimetric Methods for the Determination of Iron in Waste Oils

No of Experiment	Quality of Oil	Iron in g per 1 g oil		Relative Error in %
		Introduced	Determined	
1	Avtol "6", solvent refined without any additions	0.000180	0.000174	+3.4
2	The same	0.000243	0.000249	-2.4
3	" "	0.000014	0.000014	--
4	" "	0.000083	0.000081	+2.5
5	" "	0.000186	0.000174	+6.9
6	" "	0.000252	0.000235	+7.2
7.	" "	0.000051	0.000053	-3.6
			Average	±3.7

Table 4. Determination of Lead in Artificial Mixtures After Ashing of Oil

No of Experiment	Quality of Oil	Lead in g per 1 g oil		Relative Error in %
		Introduced	Determined	
1	Avtol "10", solvent refined	0.001030	0.001070	+3.9
2	The same	0.000690	0.000690	--
3	" "	0.000350	0.000340	-2.9
4	" "	0.000200	0.000200	--
5	" "	0.000100	0.000098	-2.0
6	" "	0.000051	0.000056	+9.8
			Average	±3.1

Table 5. Determination of Copper in Artificial Mixtures After Ashing of Oil

No of Experiment	Quality of Oil	Copper in g per 1 g oil		Relative Error in %
		Introduced	Determined	
1	Avtol "10", solvent refined	0.000210	0.000210	--
2	The same	0.000127	0.000137	+8.0
3	" "	0.000097	0.000100	+3.1
4	" "	0.000063	0.000067	+6.3
5	" "	0.000031	0.000030	-3.2
			Average	±3.5

Table 6. Determination of Tin from Artificial Mixtures After its Extraction with Hydrochloric Acid

No of Experiment	Quality of Oil	Tin in g per 1 g oil		Relative Error in %
		Introduced	Determined	
1	Avtol "10", solvent refined	0.001240	0.001240	--
2	The same	0.000110	0.000120	+8.1
3	" "	0.000072	0.000063	-12.5
4	" "	0.000068	0.000062	- 8.9
5	" "	0.000060	0.000059	- 1.7
6	" "	0.000052	0.000047	- 9.6
			Average	± 6.8

Table 7. Determination of Iron, Lead, and Copper when they are Jointly Present

No of Test	Quality of Oil	Introduced in g per 1 g oil	Determined in g per 1 g oil	Relative Error in %
1	Avtol "10", solvent refined	Fe - 0.000270	Fe - 0.000290	+7.4
		Pb - 0.000250	Pb - 0.000230	-8.0
		Cu - 0.000150	Cu - 0.000150	--
2	The same	Fe - 0.000190	Fe - 0.000190	--
		Pb - 0.000300	Pb - 0.000290	-3.3
		Cu - 0.000047	Cu - 0.000047	--
3	" "	Fe - 0.000330	Fe - 0.000340	+3.3
		Pb - 0.000050	Pb - 0.000051	+2.0
		Cu - 0.000063	Cu - 0.000060	-4.8
4	" "	Fe - 0.000027	Fe - 0.000026	-3.7
		Pb - 0.000051	Pb - 0.000049	-3.9
		Cu - 0.000031	Cu - 0.000030	-3.2
5	" "	Fe - 0.001390	Fe - 0.001350	-3.0
		Pb - 0.000100	Pb - 0.000096	-4.0
		Cu - 0.000150	Cu - 0.000150	--
			Average error	Fe ±3.4 Pb ±4.2 Cu -2.6

Table 8. Determination of Lead and Tin in Artificial Mixtures After Extraction with Hydrochloric Acid

No of Experiment	Quality of Oil	Introduced in g per 1 g oil	Determined in g per 1 g oil	Relative Error in %
1	Avtol "10", solvent refined	Pb - 0.000059	Pb - 0.000059	--
		Sn - 0.000103	Sn - 0.000091	-11.6
2	The same	Pb - 0.000049	Pb - 0.000041	-16.1
		Sn - 0.000103	Sn - 0.000091	-11.6
3	" "	Pb - 0.000019	Pb - 0.000017	-10.5
		Sn - 0.000033	Sn - 0.000037	+12.1

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Table 9. Results of Analyses of Used Oils

No of Test	Quality of Oil	Obtained in g per 1 g oil 1st determination	2d determination	Difference in g
1	Avtol "10", solvent refined	Fe - 0.000012	0.000013	0.000001
		Pb - 0.000015	0.000017	0.000002
		Cu - 0.000013	0.000015	0.000002
2	The same	Fe - 0.000012	0.000012	--
		Pb - 0.000014	0.000014	--
		Cu - 0.000003	0.000004	0.000001
3	" "	Fe - 0.000067	0.000058	0.000009
		Pb - 0.000048	0.000051	0.000003
		Cu - 0.000360	0.000350	0.000010
4	" "	Fe - 0.000260	0.000260	--
		Pb - 0.000038	0.000035	0.000003
		Cu - 0.000100	0.000100	--

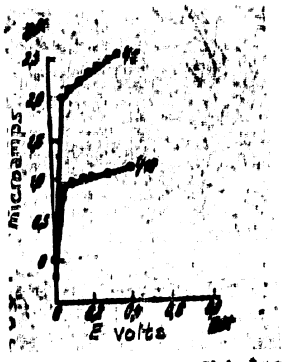

Figure 1. Polarograms of Iron Obtained After the Ashing of Avtol "10" with Iron Added

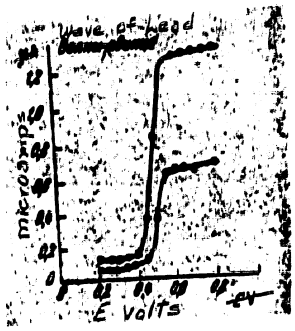

Figure 2. Polarograms of Lead Obtained After the Ashing of Avtol "10" with Lead Added

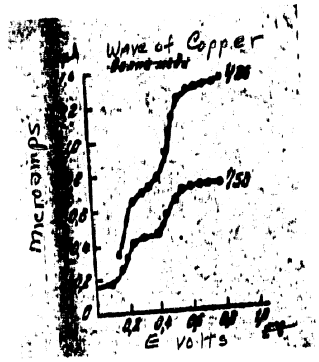

Figure 3. Polarograms of Copper Obtained after the Ashing of Avtol "10" with a Known Amount of Copper Added

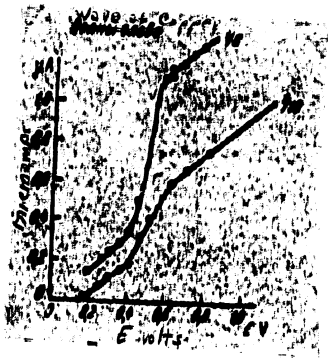

Figure 4. Polarograms of Tin Obtained After the Ashing of Avtol "10" with a Known Quantity of Tin Added